Complexes of (Phenazine)$^{-\cdot}$ and (Phenazine)$^{2-}$ with Magnesium(II): Syntheses of $[Mg(C_{12}H_8N_2)_2(thf)_3]$, $[Mg(C_{12}H_8N_2)(thf)_2]$, and $[Mg_2Br_2(C_{12}H_8N_2)(thf)_6]\cdot[MgBr_2(thf)_4]$ (thf = tetrahydrofuran) (*X*-Ray Authenticated)

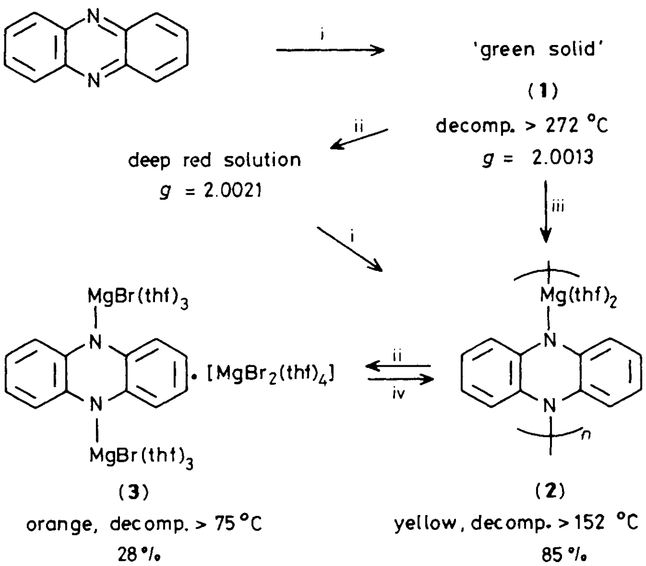
Peter C. Junk, Colin L. Raston,* Brian W. Skelton, and Allan H. White

Department of Physical and Inorganic Chemistry, University of Western Australia, Nedlands, W.A. 6009, Australia

Phenazine and magnesium in tetrahydrofuran (thf) at *ca.* 20 °C afforded a paramagnetic complex, $[Mg(C_{12}H_8N_2)_2(thf)_3]$ (**1**), and in the presence of magnesium bromide diamagnetic $[Mg(C_{12}H_8N_2)(thf)_2]$ (**2**), then $[Mg_2Br_2(C_{12}H_8N_2)(thf)_6]$ co-crystallized with $[MgBr_2(thf)_4]$ (1 : 1) (**3**); single crystal *X*-ray data revealed the phenazine-containing complex (**3**) to be monomeric, with two five-co-ordinate magnesium centres each bound to an N-centre 0.48 Å out of the 'phenazine' plane [Mg–N 2.052(7), Mg–Br 2.513(3), and Mg–O 2.066(5)—2.166(5) Å].

Polycyclic $(4n+2)\pi$ aza-compounds can form $4n\pi$ dianions with main Group 1 metals *via* electron transfer reduction involving paramagnetic radical anion species.[1,2] In the case of main Group 2 elements, in particular magnesium, only species based on radical anions are formed directly from the metal, notably $MgL_2(thf)_n$ (L = 2,2′-bipyridine[3] or 4,4′-bipyridine,[4] thf = tetrahydrofuran). Complexes based on radical anions, Mg(alkyl or aryl)L (L = 1,10-phenanthroline or 2,2′-bipyridine) are also formed on treating Grignard or magnesium dialkyl or diaryl complexes with L.[2,5] Herein we show that phenazine and activated magnesium metal in thf yield a radical anion complex then dianion-containing complexes in the presence of magnesium bromide, and report the first structure determination of a complex containing formally antiaromatic (phenazine)$^{2+}$.

Reactions are summarized in Scheme 1. A green paramagnetic material most likely of composition $[Mg(C_{12}H_8N_2)_2(thf)_3]$ (**1**)† was formed from a mixture of



Scheme 1. *Reagents and conditions:* i, Mg, thf, 20 °C, *ca.* 12 h; ii, $[MgBr_2(thf)_4]$, thf, 20 °C, *ca.* 1 h; iii, as ii plus Mg, *ca.* 12 h; iv, benzene, 20 °C.

---

† Analytical data for (**1**) were unreliable but the ratio of phenazine to thf was consistently 2 : 3, established by ^1H n.m.r. data on solutions obtained on its decomposition in carbon tetrachloride. Complexes (**2**) and (**3**) gave satisfactory analytical data.

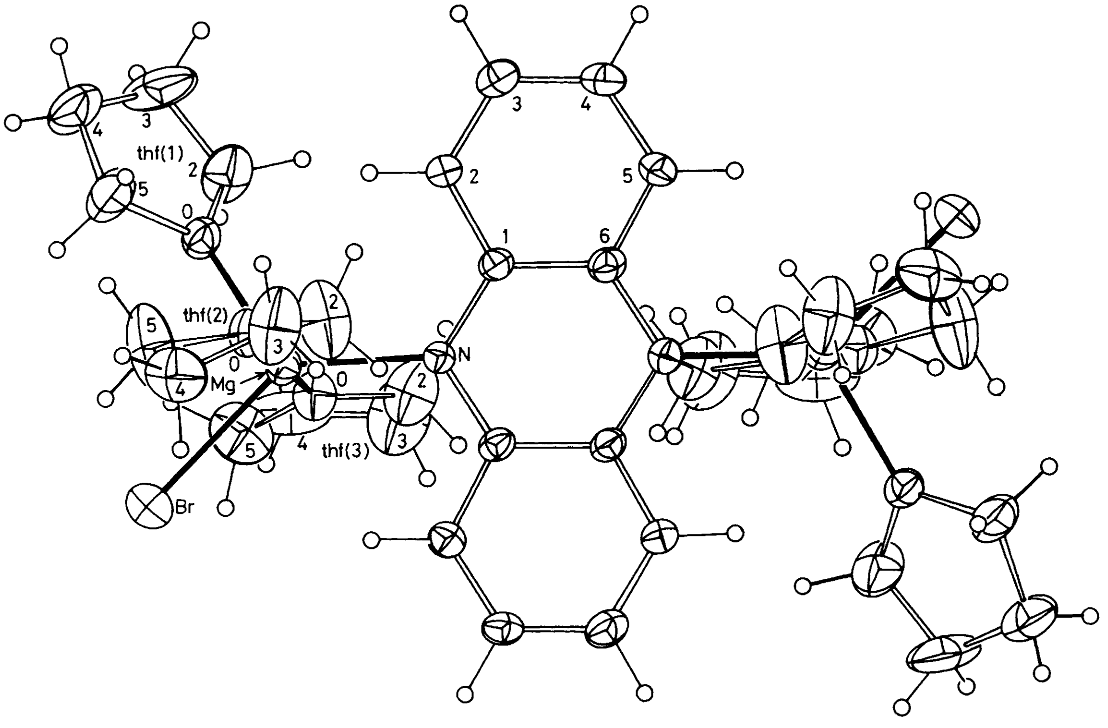


Figure 1. Molecular projection of the phenazine-containing complex $[Mg_2Br_2(C_{12}H_8N_2)(thf)_6]\cdot[MgBr_2(thf)_4]$ (**3**), showing the atom labelling scheme and 20% thermal ellipsoids for the non-hydrogen atoms, and arbitrary radii for hydrogen atoms. Selected bond distances (Å) and angles (°) are Mg–N 2.052(7), Mg–Br 2.513(3), Mg–O(1,2,3) 2.066(5), 2.166(5), and 2.115(5), N–C(1) 1.396(8), N–C(6) 1.384(7); N–Mg–Br 135.9(1), N–Mg–O(1) 119.6(2), N–Mg–O(2) 90.3(2), N–Mg–O(3) 91.0(3), Br–Mg–O(1) 104.5(2), Br–Mg–O(2) 89.6(2), Br–Mg–O(3) 90.4(2), O(1)–Mg–O(2) 90.7(2), O(1)–Mg–O(3) 87.5(2), O(2)–Mg–O(3) 178.2(2); for $[MgBr_2(thf)_4]$ Mg–Br 2.656(1), Mg–O(thf) 2.095(5) and 2.116(6); Br–Mg–Br 180(–), Br–Mg–O(thf) 89.7(1) and 90.3(1), O(thf)–Mg–O(thf) 180(–) or 89.9(2) and 90.1(2).

phenazine and magnesium in thf. Magnesium bromide (*ca.* 1 equiv.), either added to the reaction mixture or formed *in situ* from 1,2-dibromoethane and magnesium, caused rapid dissolution of (**1**), yielding deep red solutions containing persistent radicals. These slowly reacted with magnesium affording sparingly thf-soluble and diamagnetic $[Mg(C_{12}H_8N_2)(thf)_2]$ (**2**). The complexes (**1**) and (**2**) respectively contain radical anions and dianions of phenazine; two-electron reduction of phenazine has previously been achieved only electrochemically.[6] The complex (**2**) in the presence of an excess of magnesium bromide yielded a further product (**3**) consisting of the moderately thf-soluble $[Mg_2Br_2(C_{12}H_8N_2)(thf)_6]$, still based on the dianion of phenazine, co-crystallized with $[MgBr_2(thf)_4]$ in the ratio 1:1; attempts to prepare the magnesium–bromide–phenazine complex free of $[MgBr_2(thf)_4]$ were unsuccessful. Addition of benzene to (**3**) resulted in decomposition to (**2**).

The resistance of (**1**) to reaction with magnesium to form a complex based on the dianion rather than the monoanion of phenazine may be a consequence of its very low solubility in thf and/or that the phenazine is 'locked-up' by complexation to magnesium; if electron transfer forms initially 'Mg^{2+}–$C_{12}H_8N_2{}^{2-}$', subsequent complexation of phenazine to the same metal centre is likely to result in conproportionation to give (phenazine)$^{-\bullet}$. Interestingly, the reaction of isoelectronic anthracene with magnesium in thf yields a dianion- rather than a radical-anion-containing complex, $[Mg(anthracene)(thf)_3]$;[7] radical anion complexes are formed on treating this complex with anthracene and magnesium halides[8,9] or elemental magnesium and anthracene (1:2) with an excess of magnesium halide in thf.[9]

Activated magnesium in contact with a solution of phenazine and magnesium bromide in thf over *ca.* 2 months yielded (**2**) as a yellow powder, and orange crystals of (**3**) suitable for *X*-ray crystallography.‡ The $C_{12}H_8N_2$ unit is close to planar and bound through the N-centres to trigonal bipyramidal magnesium atoms (Figure 1). The molecule (**3**) can be considered as a magnesium amido complex by assuming the charge density to be predominantly on the N-centres. In accordance with this are long N–C distances [1.396(8) and 1.384(7) Å] relative to free phenazine (*ca.* 1.35 Å).[10] The Mg–N distances [2.052(7) Å] are intermediate for established terminal [1.997(7) Å][11] and bridging [2.08(1) and 2.082(7) Å][12] N-amido centres. The solvated magnesium bromide has an unexceptional *trans*-octahedral magnesium centre. By analogy with the structure of (**3**), the structure of (**2**) is most likely polymeric with the dianion spanning successive metal centres (Scheme 1).

---

‡ *Crystal data:* monoclinic, space group $C2/c$, a = 28.42(3), b = 12.571(6), c = 21.129(3) Å, β = 125.24(6)°, Z = 4, D_c = 1.39 g cm^{-3}, 2690 'observed' reflections [$(I) > 3\sigma(I)$], $2\theta_{max}$ = 50°, R = 0.052, R_w = 0.058; Mo-K_α radiation [T 295 K]. Syntex $P2_1$ diffractometer. Atomic co-ordinates, bond lengths and angles, and thermal parameters have been deposited at the Cambridge Crystallographic Data Centre. See Notice to Authors, Issue No. 1.

We thank the Australian Research Grants Scheme for support of this work.

Received, 24th February 1987; Com. 246

References

1 Y. Cohen, A. Y. Meyer, and M. Rabinovitz, *J. Am. Chem. Soc.*, 1986, **108**, 7039, and references therein.

2 W. Kaim, *J. Am. Chem. Soc.*, 1982, **104**, 3833.

3 S. Herzog and R. Taube, *Z. Chem.*, 1962, **2**, 208.

4 K. Luhder and I. Orfert, *Z. Chem.*, 1970, **10**, 32.

5 W. Kaim, *Chem. Ber.*, 1981, **114**, 3789; *Angew. Chem., Int. Ed. Engl.*, 1982, **21**, 140; *J. Organomet. Chem.*, 1981, **222**, C17; *Z. Naturforsch., Teil B*, 1981, **36**, 1110.

6 R. C. Kaye and H. I. Stonehill, *J. Chem. Soc.*, 1952, 3240.

7 B. Bogdanovic, S. Liao, R. Mynott, K. Schlichte, and U. Westeppe, *Chem. Ber.*, 1984, **117**, 1378.

8 P. K. Freeman and L. L. Hutchinson, *J. Org. Chem.*, 1983, **48**, 879.

9 B. Bogdanovic, N. Janke, C. Kruger, R. Mynott, K. Schlichte, and U. Westeppe, *Angew. Chem., Int. Ed. Engl.*, 1985, **24**, 960.

10 A. M. Glazer, *Phil. Trans. Roy. Soc.*, 1970, **266**, 593; *cf.* also 1.33_8 and 1.34_4 Å in 1,6-dimethylphenazine (Y. Kitano, T. Ashida, and A. Yabe, *Acta Crystallogr., Sect. B.*, 1981, **37**, 1435).

11 A. W. Duff, P. B. Hitchcock, M. F. Lappert, R. G. Taylor, and J. A. Segal, *J. Organomet. Chem.*, 1985, **293**, 271.

12 (*a*) V. R. Magnuson and G. D. Stucky, *Inorg. Chem.*, 1969, **8**, 1427; (*b*) L. M. Engelhardt, B. S. Jolly, P. C. Junk, C. L. Raston, B. W. Skelton, and A. H. White, *Aust. J. Chem.*, 1986, **39**, 1337.